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STUDY OF THE PRODUCTION OF BARIUM CHEMICALS FROM THE CONWEST BARITE DEPOSIT AT LAKE AINSLIE, CAPE BRETON NOVA SCOTIA

PHASE II-B - LABORATORY INVESTIGATIONS

for

CONWEST EXPLORATION COMPANY LIMITED

by

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EXECUTIVE SUMMARY

Phase II-B of the study of the production of barium chemicals from the Conwest barite at Lake Ainslie, Cape Breton, was focused on laboratory investigations to prepare reagent-grade barium carbonate from Conwest barite black ash. Experiments were conducted with black ash prepared from a mixture of flotation concentrates containing 1.64% fluorite.

Industrial-grade barium carbonate was prepared directly from barite black ash with over 95% recovery of the barium. Reagent-grade barium carbonate was prepared from barium chloride with a recovery of barium in the reagent-grade barium carbonate of over 91%. Reagent-grade barium carbonate was obtained by first preparing barium chloride from the black ash, dissolving the barium chloride in water and carbonating the resulting solution. The barium recovered from the black ash was 91%.

Reagent-grade barium chloride and barium nitrate were prepared from Conwest barite black ash. In the preparation of barium chloride 77% of the barium was recovered in the product. In preparing barium nitrate 83% of the barium was recovered. The preparation of these two reagent-grade products depends on the ratio of solids to mother liquor after evaporation. The quantity of the contaminant, strontium, separated from the barium is proportional to the final volume of liquor.

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INTRODUCTION

Concentrates of the Conwest Barite Deposit at Lake Ainslie, prepared at the Minerals Engineering Centre, Technical University of Nova Scotia, were the feedstocks to evaluate the suitability of this ore as a source of barium for barium chemicals production. The first concern addressed was that the presence of fluorite in the concentrates may impair the reduction process and produce environmental pollutants such as hydrofluoric acid and fluorocarbons. In addition there was concern that if hydrofluoric acid was produced it would damage conventional kiln refractory linings. During Phase IIA of the "Study of the Production of Barium Chemicals from the Conwest Barite Deposit at Lake Ainslie, Cape Breton, Nova Scotia"[1] it was demonstrated that over 90% of the barium can be recovered from the barite via the black ash process provided the barite is beneficiated to less than 1.5% fluorite. It was also shown that fluorite present in the barite yields some hydrofluoric acid in the high temperature reduction of barium sulphate. Apparent deterioration of the firebrick used in the experimental trials was attributed to the presence of fluorite in the ore concentrates.

Since over 90% of the barium in the Conwest beneficiated barite reports to the black ash leachate, laboratory test work, Phase IIB, was initiated to evaluate the role of impurities on purity of barium carbonate produced by this process. Phase IIB of this project is concerned with the production of commercial grade barium carbonate from black ash prepared from chemical grade French, flotation beneficiated and table beneficiated Conwest barite. Barium carbonate is to be prepared from each sample of black ash and analyzed to determine the degree of contamination by the extraneous components in the black ash.

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[1] Lutwick, G.D., "Study of the Production of Barium Chemicals From the Conwest Barite Deposit at Lake Ainslie, Cape Breton, Nova Scotia, Phase IIA - Laboratory Investigations", June, 1989.

Assuming the barium carbonate does not meet commercial standards, experiments based on differences in solubility of components will be designed and conducted to produce an acceptably pure product.

EXPERIMENTAL

The samples of black ash for this phase of the project were prepared from barite concentrates and coke used in Phase II-A. A complete analysis of the four barite samples and the flotation mix concentrate is presented in Table 1. These results compare favourably with the results reported in Phase II-A, Table 1, for the Chemical Grade French and the Table Concentrate. A higher value for $BaSO_4$ was obtained in the Flotation Mix Concentrate. This value is more realistic as it corresponds closely to the value calculated from the composition of the component barites.

TABLE 1

ANALYSIS OF BARITE SAMPLES

Component	Table Concentrate (No. 23)	Flotation Concentrate (No. 1)	Flotation Concentrate (No. 8)	Flotation Mix Concentrate (Nos. 1 & 8)	Chemical Grade French
	%	%	%	%	%
$BaSO_4$	94.47	97.10	82.39	95.39	98.15
$SrSO_4$	2.56	2.79	3.03	2.83	0.80
CaF_2	1.59	0.55	7.63	1.64	0.05
SiO_2	0.28	0.35	4.46	0.47	0.23
Al_2O_3	0.03	0.07	0.22	0.08	0.11
Fe_2O_3	0.04	0.02	0.07	0.03	0.006
K_2O	0.02	0.01	0.05	0.02	0.02
MgO	0.01	0.001	0.05	0.02	ND
MnO	0.003	ND	0.08	0.002	ND
	ppm	ppm	ppm	ppm	ppm
Cu	7	ND	37	10	ND
Pb	ND	ND	30	ND	ND
Cd	3	ND	ND	ND	ND
Na	ND	ND	ND	ND	ND

PREPARATION OF BLACK ASH

A quantity of black ash was prepared from the barites by reduction with coke mixed in the ratio of 5:1.2 by weight at 1250°C. The size of the reduction furnace limited the size of charge to 100 g, hence a number of charges were reduced to obtain sufficient black ash for the study of black ash conversion to barium carbonate. The percent of the barium converted to water leachable barium sulphide in each charge is reported in Table 2. The results in Table 2 show a consistent yield of leachable barium in the black ash for the charges of each barite sample. The average values are 95.29% for the chemical grade French, 94.57% for the Table Concentrate (No. 23) and 94.13% for the Flotation Mix Concentrate. (Nos. 1 and 8).

The individual reduced charges of the barites were combined forming composite black ash samples of the three barites. The black ash samples were analyzed and the results reported in Table 3. The quantitative data developed in the conversion of black ash to barium carbonate are based on these values.

TABLE 2

PRODUCTION OF LEACHABLE BARIUM BY BARITE REDUCTION WITH COKE

Barite to Coke Ratio 5:1.2

	% Ba Leached		
	Chemical Grade French	Table Concentrate (No. 23)	Flotation Concentrate Mix (92% No. 1 & 8% No. 8)
1	93.52	95.80	90.98
2	95.58	93.86	94.82
3	94.05	95.43	95.01
4	97.31	93.65	94.25
5	95.36	95.30	94.93
6	95.98	94.42	94.98
7	93.02	93.59	94.92
8	96.74	94.53	93.21
9	97.31		
10	94.04		
Average	95.29	94.57	94.13

TABLE 3

ANALYSIS OF COMPOSITE BLACK ASH SAMPLES

Component	Chemical Grade French %	Table Concentrate (No. 23) %	Flotation Mix Concentrate (FC-1 to 8 Blend) (92% No. 1 + 8% No. 8) %
Ba	66.09	62.43	64.90
Sr	0.38	1.25	1.52
Ca	0.26	1.54	1.77
Si	0.25	0.33	0.33
F	0.02	0.41	0.70
Al	0.07	0.08	0.08
Fe	0.15	0.15	0.15
Na	0.08	0.08	0.08
Mn	ND	ND	ND
Cu	ND	ND	ND
Pb	ND	ND	ND
Cd	ND	ND	ND
	ppm	ppm	ppm
K	241	253	247
Mg	24	47	43

PREPARATION OF SUPPLEMENTARY BLACK ASH

The quantity of original black ash prepared from Conwest Lake Ainslie beneficiated barite was insufficient to complete this program. A second batch was prepared from the flotation mix concentrate by reducing at 1250°C four charges prepared as the original charges. The analysis of the resulting black ash composite, for the major contaminants is given in Table 4.

TABLE 4

ANALYSIS OF FLOTATION MIX CONCENTRATE BLACK ASH BLENDS FC-9 TO FC-12

Component	Wt. %
Ba	63.12
Sr	1.54
Ca	1.32
Fe	0.15
F	0.82

PREPARATION OF BARIUM CARBONATE

Barium carbonate was prepared from the composite black ash samples, Table 3, by the method of industry. This required leaching of the black ash at 80°C, filtration to separate the insoluble material, followed by the addition of sodium carbonate. Barium carbonate precipitated from solution, filtered and dried. Table 5 contains the analytical results for these products and provides reference values for the following barium carbonate purification studies. A semi-quantitative spectrographic analysis, Table 6, of the carbonate products agrees with the results reported in Table 5. The material balance data for these three products are given in Tables B-1, B-2 and B-3 in Appendix B. Comparison of the data in Table 5 with the specification data of Table 7 indicates the product meets industrial-grade specifications. The production of reagent-grade barium carbonate from Conwest Lake Ainslie barite requires a means of reducing the quantity of strontium and calcium reporting to the barium carbonate. The following experiments address this possibility.

Application of NaOH

The solubilities of barium sulphide, barium hydrogen sulphide, barium hydroxide, strontium hydrogen sulphide and strontium hydroxide as a function of temperature are depicted in Figure 1. The main feature of this data is the greater solubility of barium compounds in relation to the corresponding strontium compounds. Calcium hydroxide is much less soluble than strontium hydroxide hence is not plotted. This information suggests that calcium and

strontium may be removed with the water insolubles from the black ash leachate as their hydroxides prior to the formation of barium carbonate.

The addition of sodium hydroxide to the leachate reduced the percent calcium in the barium carbonate by 75% with no effect on the percent strontium. This reduction in % calcium in the product is temperature dependent, decreasing as the temperature of carbonation decreases from 80°C to 10°C.

The beneficial effect of sodium hydroxide is not sufficient to produce a reagent-grade product although the calcium, 0.07%, is close to the specified value of 0.05%. The addition of sodium hydroxide to the leaching step produces a small increase in fluoride reporting to the barium carbonate.

A number of runs, in which the black ash leachate was treated with various amounts of sodium hydroxide and at different temperatures, were studied and the resulting barium carbonates analyzed. The analysis of the barium carbonates are listed in Table 8. The corresponding material balance data is given in the Appendix Tables B-4, B-5, B-6, B-9 and B-11.

TABLE 5

ANALYSIS OF $BaCO_3$ PRODUCED FROM COMPOSITE BLACK ASH SAMPLES

Component	Chemical Grade French %	Table Concentrate (No. 23) %	Flotation Mix Concentrate (92% No. 1 + 8% No. 8) %
$BaCO_3$	97.11	96.16	97.10
Sr	0.33	1.44	1.43
Ca	0.15	0.16	0.23
Si	0.08	0.04	0.04
F	0.02	0.06	0.04
Na	0.28	0.25	0.26
Al	ND	ND	ND
Fe	ND	ND	ND
Mn	ND	ND	ND
Cu	ND	ND	ND
Pb	ND	ND	ND
Cd	ND	ND	ND
	ppm	ppm	ppm
K	127	116	127
Mg	14	11	8

TABLE 6

SPECTROGRAPHIC ANALYSIS OF BARIUM CARBONATES

Black Ash Sample	%				
	0.0001-0.001	0.001-0.01	0.01-0.1	0.1-1.0	+1.0
Chemical Grade French	Cu	Mg, Al	Si	Ca, Sr, Na	Ba
Table Concentrate #23	Cu, Al	Si, Mg	-	Ca, Sr, Na	Ba
Flotation Mix Concentrate (92% No. 1 + 8% No. 8) (FC-1 to 8 Blend)	Cu	Si, Mg, Al	-	Ca, Sr, Na	Ba

No analysis for K and Li used in buffer. If not listed, not detected. If present less than:

<1.0%	P
<0.1%	Cd, As, W, Ta, Na
<0.05%	Zn, U
<0.033%	Th, Ce, Tl
<0.01%	Sn, Mo, Ge, In, Bi, Nd, Nb, Sb, B, Pb, Zr, Fe
<0.005%	Ga, La
<0.001%	Mn, V, Yb, Y, Cr, Ti, Ni, Co
<0.0001%	Ag, Sc, Be

TABLE 7

SPECIFICATIONS FOR REAGENT-GRADE BARIUM CARBONATE

Insoluble in Dilute HCl, % Max.	0.015
Chloride, % Max.	0.002
Hydroxide and Alkali Carbonate	To Pass Test
Oxidizing Substances (As NO_3), % Max.	0.005
Sulphide (Limit About 0.001%)	To Pass Test
Substances Not Precipitated by H_2SO_4, % Max.	0.25
Calcium, % Max.	0.05
Heavy Metals (As Pb), % Max.	0.001
Iron, % Max.	0.002
Strontium (Limit About 0.3%)	To Pass Test

TYPICAL SPECIFICATIONS FOR INDUSTRIAL-GRADE BARIUM CARBONATE

Barium and Strontium (As $BaCO_3$), %	98.0
Moisture, %	0.15
Loss on Ignition, %	1.00
Acid-Insoluble Residue, %	0.70
Sodium Sulphide, %	0.10
Sulphur Dioxide, %	0.10
Calcium Plus Strontium, %	2.00
Iron	70 ppm

Source: Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, D. C., 1960

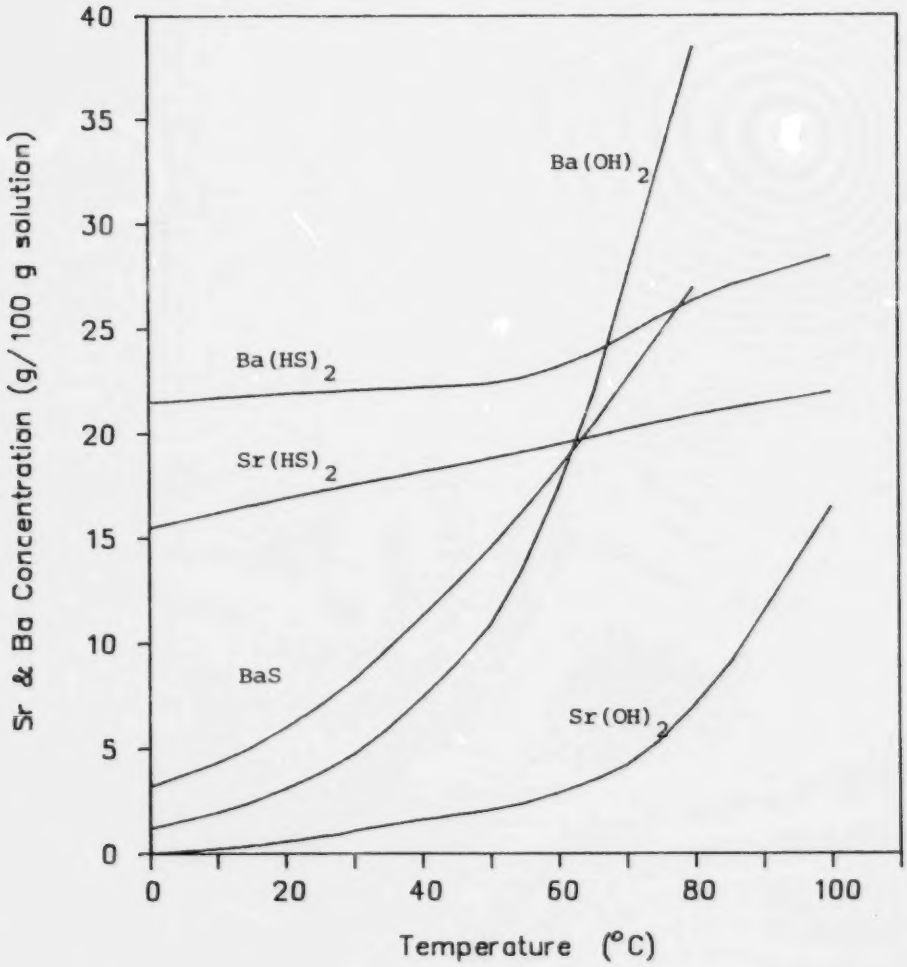

Figure 1, Solubilities of Barium and Strontium Compounds as a Function of Temperature

TABLE 8

PURIFICATION OF BARIUM CARBONATE BY SODIUM HYDROXIDE ADDITION TO THE BLACK ASH LEACHATE

	Untreated Leachate	0.5 g NaOH	1.13 g NaOH	1.69 g NaOH	1.19 g NaOH	1.24 g NaOH
Run #:	BC-2	BCP-1	BCP-2	BCP-3	BCP-6	BCP-9
Component	Wt %	Wt %	Wt %	Wt %	Wt %	Wt %
Ba	68.18	66.03	66.37	64.70	66.16	66.10
Sr	1.43	1.30	1.30	1.30	1.38	1.40
Ca	0.23	0.065	0.069	0.056	0.09	0.22
F	0.04	0.06	0.07	0.07	0.06	0.07
% Recovery in $BaCO_3$	96.67	93.47	91.31	90.90	87.76	60.87

Black Ash from Flotation Mix Concentrate FC-1 to 8 Blend
Na_2CO_3 Source of $CO_3^=$

Runs BC-2, BCP-1, 2, 3 $BaCO_3$ precipitated at 80°C

Runs BCP-6 and 9 $BaCO_3$ precipitated at 40°C and 10°C respectively.

Comparison of percent barium recovered in the barium carbonates produced from the hydroxide treated leachates with the barium carbonate from untreated leachates, Run BC-2, shows a 1.8 to 3.5% decrease in % barium. This decrease is dependent of the quantity of sodium hydroxide added and the temperature of precipitation of the barium carbonate. The material balance data shows that in sodium hydroxide treated leachates a larger quantity of barium remains in the barren solution than in the barren of untreated leachates, i.e. barium carbonate increases in solubility in the presence of sodium hydroxide. This increase in barium carbonate solubility accounts for the decrease in recovery of barium as the carbonate with increasing amounts of sodium hydroxide added to the leach liquor.

Separation of Strontium and Calcium From Black Ash Leach Liquors By Means Other Than Sodium Hydroxide

The greater solubility of barium carbonate compared with strontium and calcium carbonates suggests that purified barium carbonate may be produced by the primary addition of carbonate sufficient to precipitate the strontium and calcium followed by filtration and then precipitation of the barium in the filtrate. The analysis of a product produced by this means is given in Table 9 under the heading Run BCP-5. Comparison of the wt % compositions with Run BC-2, shows a reduction in the strontium and calcium reporting to the barium carbonate. The reduction in percent calcium is small compared to the reduction realized with sodium hydroxide.

Preferential precipitation of the strontium and calcium by means of homogeneous precipitation was attempted with urea. Urea is soluble in water and decomposes when heated yielding ammonia and carbon dioxide. Carbon dioxide reacts to form carbonate in an alkaline aqueous solution and thus precipitates insoluble carbonates throughout the solution. The reaction was carried out with a black ash leachate at 80°C with sufficient urea to precipitate the strontium and calcium. The primary precipitate was separated from the mother liquor with the black ash residue. The mother liquor was carbonated with sodium carbonate to precipitate the barium. The analysis of the resulting barium carbonate is given in Table 9, Run BCP-7. Comparison of the strontium and calcium values with the values for Run BC-2 shows that homogeneous precipitation with urea does not preferentially precipitate strontium and calcium from solution in the presence of barium.

Direct carbonation of black ash leachate with carbon dioxide did not improve the barium carbonate product. Barium carbonate was precipitated by means of carbon dioxide addition at two temperatures, 80°C and 8°C. The analysis of the resulting products are given in Table 9 under the headings BCP-15 and BCP-16 respectively. The percent strontium and calcium correspond with precipitation by means of sodium carbonate, Run BC-2.

The influence of quantity of carbon dioxide added to the leachate was investigated. The analysis of the resulting barium carbonate products, Table 10, Runs BCP-11 to BCP-14, shows that excess carbon dioxide does not significantly influence the composition of the resultant barium carbonate. The black ash used for the runs reported in Table 10 was Table # 23 concentrate which was similar to the Flotation Mix Concentrate. This change was necessary

while a new composite of the Flotation Mix Concentrate black ash used in the previous experiments was being analyzed and blended. (FC-9 to 12 Blend).

TABLE 9

PURIFICATION OF $BaCO_3$ BY VARIOUS MEANS

	Untreated Leachate	1.21 g Na_2CO_3	1.05 g Urea	CO_2 @ 80°C	CO_2 @ 8°C
Run #:	BC-2	BCP-5	BCP-7	BCP-15	BCP-16
Component	Wt %	Wt %	Wt %	Wt %	Wt %
Ba	68.18	65.89	65.61	68.40	64.41
Sr	1.43	1.30	1.40	1.43	1.37
Ca	0.23	0.19	0.25	0.13	0.23
F	0.04	0.07	0.07	0.09	0.14

METHOD DESCRIPTION:

BC-2	Untreated Leachate. $BaCO_3$ Precipitated @ 80°C Using Na_2CO_3.
BCP-5	1.25 gms Na_2CO_3 added to leachate to precipitate Sr and Ca. Precipitated $BaCO_3$ using Na_2CO_3 @ 80°C.
BCP-7	1.05 gms urea to leachate to precipitate Sr and Ca. $BaCO_3$ precipitated using Na_2CO_3 @ 80°C.
BCP-15	Direct carbonation of leachate @ 80°C using CO_2.
BCP-16	Direct carbonation of leachate @ 8°C using CO_2.

TABLE 10

PRODUCTION OF $BaCO_3$ FROM TABLE # 23 CONCENTRATE USING CARBON DIOXIDE

	Untreated Leachate	4.46 g CO_2	5.23 g CO_2	10.45 g CO_2	20.91 g CO_2
Run #:	BC-3	BCP-11	BCP-12	BCP-13	BCP-14
Component	Wt %	Wt %	Wt %	Wt %	Wt %
Ba	67.13	68.28	67.73	67.73	67.23
Sr	1.44	1.45	1.46	1.42	1.40
Ca	0.16	0.12	0.10	0.12	0.10
F	0.06	0.07	0.07	0.06	0.05

METHOD DESCRIPTION:

BCP-11, 12, 13 & 14: Direct Carbonation of Leachate @ 45 - 50°C Using CO_2 @ 1 L/min.
BC-3: $BaCO_3$ Precipitated at 80°C Using Na_2CO_3.

PURIFICATION BY RECRYSTALLIZATION OF BARIUM SULPHIDE

The removal of Sr and Ca in the black ash leachate was attempted by recrystallization of the barium sulphide. The percent strontium and calcium found in the products for three successive recrystallizations are given in Table 11. The concentrations in the original black ash are given for comparison. The results indicate that a reduction had occurred in the first recrystallization while increasing in the second. The experiment was repeated, Run BSP-2, with the same result. The runs were repeated at different temperatures of crystallization, i.e. 10°C, 15°C, 20°C. The results are reported in Table 12.

When barium sulphide is dissolved in water the sulphide ion hydrolyzes forming hydrogen sulphide and hydroxyl ions. When such a solution is cooled or evaporated the precipitate would not be barium sulphide, as in the black ash but a mixture of barium hydroxide and barium sulphide.

Recrystallization of Barium Sulphide

The formation of barium hydroxide with cooling promotes the formation of calcium hydroxide, a product more insoluble than barium hydroxide. This promotion of calcium hydroxide formation would result in separation of calcium as a precipitate. The same would occur with strontium but not to the same extent, as strontium hydroxide is more soluble than calcium hydroxide. The phenomenon is supported by the results reported in Table 12 in which

the calcium is reduced to 0.01% and the strontium to 0.81% to 0.98%. Reduction of strontium and calcium in black ash leach solution by recrystallization was confirmed by analyzing the barium carbonate produced after one recrystallization. The results of duplicate runs, BSP-7 and BSP-8, are reported in Table 13. Comparison of these values with the values obtained with unpurified black ash shows a marked decrease in concentration of calcium to less than the specification value of 0.05% for reagent-grade barium carbonate. The reduction in strontium was not as significant.

The material balance data for runs BSP-7 and BSP-8, Tables B-18 and B-19 in the appendix show that 48.11% and 56.24% of the barium in the black ash reported as barium carbonate using recrystallization as a means of purification.

TABLE 11

PURIFICATION OF BARIUM SULPHIDE

USING FLOTATION CONCENTRATE MIX

Component	Black Ash Wt %	Run BSP-1 ------Purified BaS------ 1 Wt %	2 Wt %	3 Wt %	Run BSP-2 ------Purified BaS------ 1 Wt %	2 Wt %	3 Wt %
Sr	1.52	-	0.86	0.74	0.53	0.97	0.71
Ca	1.77	-	0.01	0.01	0.01	0.01	0.01

TABLE 12

PURIFICATION OF BARIUM SULPHIDE

USING TABLE # 23 CONCENTRATE MIDDLE # 1 AND # 2

Component	Black Ash	Purified BaS		
		BSP-3 Temp 15°C	BSP-4 Temp 20°C	BSP-5 Temp 10°C
Sr	1.25	0.98	0.91	0.81
Ca	1.54	0.01	0.01	0.01

TABLE 13

BARIUM CARBONATE FROM RE-PRECIPITATED BARIUM SULPHIDE

Components	$BaCO_3$ From Unpurified Black Ash BC-3	$BaCO_3$ From Purified Black Ash	
		BSP-7	BSP-8
Ba	67.13	69.10	68.83
Sr	1.44	1.16	1.15
Ca	0.16	0.04	0.02

Black Ash from Bulk Table # 23 Concentrate Middle # 1 and # 2

PREPARATION OF BARIUM CHLORIDE

Barium chloride was prepared from black ash by addition of sodium chloride or concentrated hydrochloric acid to the black ash leachate. The barium product was obtained by evaporation of the water followed by filtration of the solid. The method description is in Appendix A. The Material Balance Data is recorded in Appendix B.

The preparation of barium chloride by sodium chloride addition formed an undefined precipitate. The percent barium, Table 14, $BaCl_2 \cdot 2H_20$ Run # 1, in this product was 35.34%; low for barium chloride compared to the theoretical value of 56.22%, and was assumed to form, by salting out, a mixture of barium hydroxide, barium sulphide and barium chloride.

The products in $BaCl_2 \cdot 2H_20$ Runs # 2, 3, 4, 5, 6 and 7 were prepared from black ash leach solution and concentrated hydrochloric acid. In Runs 2 and 5, in which the resulting solutions were evaporated to dryness, the leachable strontium reports to the product. Comparing these results with Run 4, the volume of solution was reduced by 95% and then filtered. The weight % strontium in the product was 0.20%. This is in excess of the limit of about 0.10% required for reagent-grade barium chloride.

Evaporation of the resulting barium chloride solution to about 7% of the original volume and then separating the solids by filtration provided products containing 0.01 and 0.06% strontium. The analysis of two runs is given in Table 14, $BaCl_2 \cdot 2H_20$ Runs 6 and 7. The analytical results for strontium, calcium and iron satisfy the specifications for reagent-grade

barium chloride. The specifications for reagent-grade barium chloride, published by the American Chemical Society is given in Table 15.

TABLE 14

ANALYSIS OF $BaCl_2 \cdot 2H_2O$ PRODUCTS

	$BaCl_2 \cdot 2H_2O$ Runs						
Run No: Component	1* Wt. %	2 Wt. %	3 Wt. %	4 Wt. %	5 Wt. %	6 Wt. %	7 Wt. %
Ba	35.34	58.60	58.70	58.25	59.78	58.15	57.54
Sr	0.25	1.24	0.25	0.20	1.31	0.01	0.06
Ca	0.06	0.06	0.01	0.01	0.11	ND**	ND
Fe	ND	ND	ND	ND	ND	ND	ND
F	0.09	0.02	0.01	0.01	0.01	0.002	0.004
Na	2.53	0.02	0.03	0.09	0.04	0.03	0.03
% Ba Recovered as $BaCl_2 \cdot 2H_2O$	34.33	100.82	88.21	92.65	96.96	59.70	77.31

Material Balance Data in Appendix B Tables B-20, B-21, B-22, B-23, B-24, B-25, B-26

*1. Prepared by addition of NaCl to leachate
2. Prepared by addition of conc. HCl, evaporated to dryness
3. Prepared by addition of conc. HCl, 95% of solution evaporated off
4. Prepared by addition of conc. HCl, 95% of solution evaporated off
5. Repeat of 2, evaporated to dryness
6. Prepared by addition of conc. HCl, 94% of solution evaporated off
7. Prepared by addition of conc. HCl, 92% of solution evaporated off

** ND - Not Detected

TABLE 15

SPECIFICATIONS FOR REAGENT-GRADE BARIUM CHLORIDE

$BaCl_2.2H_2O$

Insoluble Matter, % Max.	0.005
pH of a 5% solution at 25°C	5.2 - 8.2
Oxidizing Substances (As NO_3), % Max.	0.005
Substances Not Precipitated by Sulphuric Acid, % Max.	0.050
Calcium, % Max.	0.05
Heavy Metals (As Pb), % Max.	0.0005
Iron, % Max.	0.0002
Strontium	To Pass Test (limit about 0.10%)

Source: Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, D.C., 1960, p. 89

PREPARATION OF BARIUM CARBONATE FROM BARIUM CHLORIDE

Barium chloride, prepared by the addition of hydrochloric acid to Conwest barite black ash leachate, has been analyzed and is a reagent-grade product with reference to strontium and calcium. Hence, the barium chlorides prepared in $BaCl_2 \cdot 2H_20$, Runs 4 and 5, were converted by sodium carbonate as a means of preparing reagent-grade barium carbonate. The material balance data for these runs are contained in Appendix B, Tables B-23 and B-24, under the heading Material Balance Data (B). The data shows 98% of the barium in the barium chloride is converted to barium carbonate and 75 and 95% of the strontium accompanies the barium carbonate. The high strontium recoveries indicate that to obtain a reagent-grade barium carbonate via barium chloride the strontium must be separated in preparing the barium chloride.

The analysis of the barium carbonate products are given in Table 16 under the headings of $BaCl_2 \cdot 2H_20$, Runs 4 and 5. The difference in percent strontium in the two products originates from the difference in strontium in the barium chlorides. The limit for strontium in reagent-grade is about 0.3%. Strontium in the barium carbonate prepared in Run # 4 satisfies this specification. The specifications for calcium and iron are also satisfied. Reagent-grade barium carbonate can thus be prepared from the Conwest Lake Ainslie barite via barium chloride provided in the preparation of barium chloride, the mother liquor is evaporated to about 7% of the original volume.

TABLE 16

ANALYSIS OF $BaCO_3$ PREPARED FROM $BaCl_2 \cdot 2H_2O$

Component	$BaCO_3$ From $BaCl_2 \cdot 2H_2O$ # 4 Wt. %	$BaCO_3$ From $BaCl_2 \cdot 2H_2O$ # 5 Wt. %
Ba	63.02	66.50
Sr	0.16	1.43
Ca	0.01	0.11
Fe	ND	ND
F	0.01	0.01
Na	0.26	0.34

PREPARATION OF BARIUM NITRATE

Barium nitrate was prepared by the addition of concentrated nitric acid to a slurry of industrial grade barium carbonate prepared in Run BCP-9. The barium salt was formed by evaporation to near dryness and separated from the solution by filtration. The analysis of the resulting product is given in Table 17, Run $Ba(NO_3)_2$ # 2. Barium nitrate was also prepared by addition of concentrated nitric acid to black ash leachate from flotation concentrate mix FC-9 to 12 Blend. The analysis of the products obtained from leachate, with evaporation to different volumes of liquid phase are in Table 17, Runs $Ba(NO_3)_3$ # 2 to $Ba(NO_3)_2$ # 5.

The barium and nitrate analysis in these products are similar to the theoretical values of 52.55% and 47.45% respectively. The final volume of residual solution after evaporation influences not only the percent barium recovered but also the concentration of strontium in the product for Runs $Ba(NO_3)_2$ # 2, # 3 and # 5, while the strontium content in $Ba(NO_3)_2$ # 4, which was evaporated to dryness, shows that a certain quantity of supernatant solution must be present after the evaporation step to obtain a reagent-grade product.

The products from Runs $Ba(NO_3)_2$ # 3 and # 5 are within specifications for strontium, calcium, iron, heavy metals (as Pb) and chloride for reagent-grade barium nitrate. The specifications for reagent-grade barium nitrate are listed in Table 18.

TABLE 17

ANALYSIS OF $Ba(NO_3)_2$ PRODUCTS

Run No:	$Ba(NO_3)_2$ # 2	$Ba(NO_3)_2$ # 3	$Ba(NO_3)_2$ # 4	$Ba(NO_3)_2$ # 5
Component	Wt. %	Wt. %	Wt. %	Wt. %
Ba	54.46	51.14	48.72	49.98
Sr	0.15	0.08	1.22	0.07
Ca	0.008	0.004	0.10	ND
F	0.02	0.01	0.02	0.02
Fe	ND	ND	ND	ND
% Ba Recovered in $Ba(NO_3)_2$	90.47	87.64	93.54	82.95
Final Volume of Mother Liquor	To Near Dryness	15 ml	To Dryness	25 ml

TABLE 18

SPECIFICATIONS FOR REAGENT-GRADE BARIUM NITRATE

Insoluble Matter, % Max.	0.010
pH of a 5% solution at 25°C	5.0 - 8.0
Chloride, % Max.	0.0005
Substances Not Precipitated by Sulphuric Acid, % Max.	0.050
Calcium, % Max.	0.05
Heavy Metals (As Pb), % Max.	0.0005
Iron, % Max.	0.0002
Strontium	To Pass Test (limit about 0.05%)

Source: Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, D.C., 1960, p. 96

CONCLUSIONS

- Industrial-grade barium carbonate can be prepared from black ash prepared from Conwest Lake Ainslie barite.

- Over 95% of the barium in the black ash is recovered as industrial-grade barium carbonate.

- Over 91% of the barium in the black ash is recovered as reagent-grade barium carbonate, with reference to strontium and calcium by carbonating barium chloride prepared from Conwest Lake Ainslie barite.

- Reagent-grade barium chloride and barium nitrate can be prepared from Conwest Lake Ainslie barite by acidification of the resulting black ash.

RECOMMENDATIONS

- Continue with development to commercialize the production of barium chemicals from the Conwest Lake Ainslie barite deposit.

- Scale up experiments to obtain data on the influence of size on purity of product.

- Investigate recycling of waste streams from evaporators in barium chloride and barium nitrate processes.

APPENDIX A

EXPERIMENTAL PROCEDURES

Experimental Reduction Procedure

A sample of barite and coke were mixed in the weight ratio of 5:1.2 in a mixing jar. The sample was mixed on a roller mill for fifteen minutes reversing direction once during that time period. A sample, 100 g, was transferred to a reaction boat made from Krial 50 firebrick. Two reaction boats were used for each run.

The reaction boats with the charges were centred in the hot zone of the tube furnace within the four foot mullite tube. The tube had a 55 mm opening at both ends. Attached to the mullite tube with glass fittings and o-rings to form an airtight seal. The nitrogen carrier gas was used to achieve a reducing atmosphere.

The reaction time was 2 1/2 hours from start of heating to the end of the run. Generally, the furnace reached reaction temperature in 105 minutes and was maintained for 45 minutes.

The power source was removed after 2 1/2 hours. The N_2 flow remained for a period of several hours during the initial cool down. The sample remained in the furnace to cool overnight. The following morning it was removed from the furnace, weighed, transferred to a sample bottle labelled black ash Run # and crushed in a spex mixer/mill.

The sample was than analyzed for Ba, Sr, Ca, Fe and F.

Barium Carbonate Production

A: FROM BLACK ASH BLENDS

Procedure

A 25.00 gram sample of the black ash blend was weighed out in a 400 ml beaker and leached with 100 mls of hot double distilled water (80°C). After a leaching period of 30 minutes the solution was filtered through a small Buchner funnel and the residue washed with three 25 ml portions of hot double distilled water. The residue was dried and saved for analysis. The volume of the leachate was measured in a graduated cylinder and recorded.

The leachate was transferred to a 1000 ml beaker and 15.6 grams of Na_2CO_3 was added in small increments with stirring. After all the Na_2CO_3 has been added, the solution was brought to boil for 15 minutes, was removed from the heat source, and the precipitate allowed to settle. The precipitate was filtered with a Buchner funnel and washed with approximately 500 mls of hot double distilled water. The precipitate was dried and saved for analysis. The volume of the filtrate (barren) was measured in a graduated cylinder and recorded. A 25 ml aliquot of the filtrate (barren) was taken and diluted to volume in a 250 ml volumetric flask for analysis.

Twenty mls of 0.02 M $PbCl_2$ was added to a 25 ml aliquot of stock solution (barren) and analyzed by A. A. for trace elements. A second 25 ml aliquot was used for fluoride analysis.

B: <u>FROM $BaCl_2 \cdot 2H_2O$</u>

A 20.00 g sample of $BaCl_2 \cdot 2H_2O$, prepared from Flotation Concentrate Mixture black ash blend FC-9 to 12 was dissolved in 100 mls of double distilled water preheated to 80°C. A 12.50 g sample of sodium carbonate was added with stirring and the precipitate filtered and washed with double distilled water at 80°C. The $BaCO_3$ was dried at 95°C and weighed.

Barium Chloride Production

Method Description For $BaCl_2 \cdot 2H_20$ # 1

A 25.00 g sample of black ash was leached with 100 mls of double distilled water at 80°C for 30 minutes. The water insoluble residue was filtered off, dried and saved. The leachate was treated with 100 mls of a saturated NaCl solution (i.e. 38.00 g) to precipitate the $BaCl_2 \cdot 2H_20$. The solution was cooled to 25°C and the resulting precipitate filtered, dried at 95°C and weighed.

Method Description For $BaCl_2 \cdot 2H_20$ # 2 to # 7

A 25.00 g sample of black ash was leached with 100 mls of double distilled water at 80°C for 30 minutes. The water insoluble residue was filtered off, dried and saved. The hot filtered leachate was treated with 30 mls of concentrated HCl. The resultant solution was evaporated to the required volume or to dryness to crystallize the $BaCl_2 \cdot 2H_20$, filtered, washed with 30 mls of acetone, dried at 95°C and weighed.

Barium Nitrate Production

Method Description

A: From $BaCO_3$ (Run # $Ba(NO_3)_2$ # 2)

A 10.00 g sample of barium carbonate (BCP-9) produced from the Flotation Mix Concentrate was added to 120 mls of 80°C double distilled water. 19 mls of concentrated HNO_3 was added with stirring to precipitate the barium nitrate. The resulting product was filtered off, dried at 95°C and weighed.

B: From Black Ash (Runs # $Ba(NO_3)_2$ # 3, 4 and 5)

A 25.00 g sample of Flotation Concentrate Mixture FC-9 to FC-12 black ash blend was leached for 30 minutes at 80°C with double distilled water. The leachate was filtered and 25 mls of concentrated HNO_3 was added with stirring. The solution was evaporated to the required volume or to dryness. The precipitate was filtered, washed with 30 mls of acetone, dried at 95°C and weighed.

Analytical Methods

Preparation of Leachate and Residue Samples

A sample of the black ash was weighed and leached with double distilled water at 80°C for 15 minutes. The sample was then vacuum filtered through a preweighed Gooch crucible and filter pad, washed with three 10 ml aliquots of 80°C double distilled water and the filtrate transferred to a volumetric flask and made up to a 250 ml volume. This solution is the leachate. The water leached residue was dried and saved for analysis.

A 50 ml aliquot of the leachate was taken for Ba analysis by sulphate precipitation.

A 25 ml aliquot of leachate was treated with 20 ml 0.02 M $PbCl_2$ solution. The solution was filtered and the filtrate made up to volume in a 100 ml volumetric flask. Appropriate dilutions were made to analyze the leachate by atomic absorption or flame emission for Ca, Fe and Sr. Fluoride was determined by selective ion electrode.

A weighed sample of the residue was ignited at > 50°C, acid leached with 10 ml of hot concentrated HCl and the Ca, Fe, Sr and Ba concentrations determined on the final 10% HCl solution. A portion of the residue was used to determine fluoride by the fluoride method.

Determination of Barium in Barium Carbonate

Sulphate Precipitation Method

1. A 1.0000 gram sample of the precipitate was weighed and transferred to a 250 ml volumetric flask using 50 mls of 10% HCl. After the sample has completely dissolved, the solution was brought up to volume with double distilled water.

2. A 50 ml aliquot of sample solution was transferred by pipet to a 400 ml beaker. The volume was made up to 100 mls with double distilled water. One ml of methyl orange was added as an indicator.

3. The pH was adjusted to the yellow color of methyl orange with conc. NH_4OH and adjusted back to pink color with 10% HCl. A two ml excess of acid was added.

4. The solution was brought to boiling and five ml of 10% H_2SO_4 was added to precipitate the barium with stirring.

5. Solutions were covered and the precipitate let stand overnight.

6. The precipitate was then collected on Whatman 42 filter paper, washed with hot water until free of Cl- as indicated by using $AgNO_3$ on filtrate.

7. The filter papers were placed in prefired, preweighed porcelain crucibles and ashed on a hot plate.

8. The samples were then ignited to $BaSO_4$ powder in a muffle furnace @ 550°C for one hour, cooled and weighed. The weight of the precipitate $BaSO_4$ plus $SrSO_4$ was determined.

$$\text{Total Ba and Sr as \% } BaCO_3 = \frac{\text{(weight of precipitate)(.8456)(100)(5)}}{\text{(weight of sample in grams)}}$$

$$\text{\% } BaCO_3 \text{ (corrected)} = \text{\% } BaCO_3 \text{ (above)} - (\text{\% Sr})(1.6848)$$

The % Sr was determined by flame emission spectroscopy.

Trace Element Analysis

Appropriate dilutions of the $PbCl_2$ treated leachate, acid leachate and fusion leachate were prepared for analysis by atomic absorption spectrophotometry.

The samples for atomic absorption/flame emission were made up in 10% HCl.

For barium and strontium analysis it was also necessary to add 0.2 g KCl/100 mls to quench interferences.

The barium was determined by flame emission spectroscopy on the acid leach samples only.

Instrument

Perkin-Elmer 560 Atomic Absorption Spectrophotometer.

Atomic Absorption/Flame Emission

Element	Symbol	(nm)	Flame	Conditions
Barium	Ba	553.6	Nitrous Oxide-Acetylene	Flame Emission
Strontium	Sr	460.7	Nitrous Oxide-Acetylene	Flame Emission
Sodium	Na	589.0	Air-Acetylene	Flame Emission
Potassium	K	766.5	Air-Acetylene	Flame Emission
Aluminum	Al	309.3	Nitrous Oxide-Acetylene	Atomic Absorption
Magnesium	Mg	285.2	Air-Acetylene	Atomic Absorption
Lead	Pb	283.3	Air-Acetylene	Atomic Absorption
Calcium	Ca	422.7	Air-Acetylene	Atomic Absorption
Iron	Fe	248.3	Air-Acetylene	Atomic Absorption
Silicon	Si	251.6	Nitrous Oxide-Acetylene	Atomic Absorption

Fluoride Determination

Fusion Method

1. Weigh 0.2500 grams of sample into nickel crucibles. Add 1.2500 grams of Flux and mix well with sample.

2. Sinter mixture over meker burner until bubbling subsides, approximately 3 to 4 minutes. Cool.

3. Add 10 ml of distilled water and let stand overnight.

4. Loosen the contents of the crucible with a small glass rod and with the use of a small plastic funnel transfer the contents of the crucible to a 100 ml volumetric flask (plastic).

5. Rinse crucible twice with 10 ml portions of H_20, and once with 10 ml of citric acid sodium citrate buffer. Add washings to flask.

6. Swirl flask to liberate CO_2 evolving from the reaction of acid and carbonate. Dilute to volume with water. Let stand for at least one half hour before making up to ensure that all CO_2 has ceased to evolve.

Determination of Fluoride

1. Transfer a 50 ml aliquot of the sample solution to a clean propylene beaker and mix with 50 ml of TISAB buffer.

2. Immerse the electrodes into the beaker and stir slowly on a magnetic stirrer for one minute. Add 1 ml of 100 ppm F^- and continue stirring for an additional three minutes. Take reading on the mv scale before adding the F^- solution and again after the three minute period.

3. After determining the difference in mv find ΔE 20°C from the known addition table.

4. Calculation:

$$\text{ppm } F^- \text{ in sample} = \frac{\text{scale reading} \times 10^4}{\text{sample weight} \times \text{aliquot}}$$

To calculate percent fluoride the result is divided by 1000.

Reagents

1. Citric acid - sodium citrate reagent: Dissolve 193.000 grams of citric acid in one liter of distilled water. Mix with an equal volume of sodium citrate solution which

is prepared by dissolving 294.000 grams of the salt in one liter of distilled water. Adjust the pH to 3.0 with 6 molar hydrochloric acid.

2. Flux: Mix two parts by weight of sodium carbonate with one part of potassium nitrate.

3. Hydrochloric acid: Mix equal volumes of concentrated acid and fluorine free water. This solution is 6 molar HC1.

4. Sodium fluoride standard solution: 1000 ug/ml F^- solution,. Dissolve 2.21 grams of reagent grade salt in one liter of distilled water. Dilute 100 ml of the above solution to one liter, this solution contains 100 ug/ml F^-. This solution is used in the determination of fluoride by specific ion electrode.

5. Sodium hydroxide: Dissolve 200.00 grams of NaOH in one liter of distilled water. This solution is 5 molar.

6. TISAB (Frant and Ross, 1968): Prepare by dissolving 171 ml of glacial acetic acid in 1500 ml of distilled water and adding 174.000 grams of sodium chloride. Add 0.900 grams of sodium citrate and adjust the pH to 5.5 with 5 molar NaOH.

<u>These solutions are all stable indefinitely</u>

7. A solution containing 100 ml of citric acid - sodium citrate reagent and 12.500 grams of flux and made up to 1000 ml with water is used to dilute samples high in fluoride. It is used where a smaller aliquot, 5 instead of 50 ml of sample, is taken for the analysis.

   This solution was found to stabilize the selective ion electrode determination when the samples were diluted with water the results were extremely erratic.

Instrument

A Corning pH/Ion Meter Model # 135 is used for fluoride analysis. The readings are taken from the millivolt scale and are determined with the use of a reference electrode and a fluoride selective ion electrode.

References

Ward, "New and Refined Methods of Trace Analysis Useful in Geochemical Exploration", Geological Survey Bulletin 1408, pp. 77 - 84.

Snell & Hilton, Barium, Encyclopedia of Industrial Chemical Analysis, Interscience publishers, John Wiley and Sons, New York, 1968, Volume 6, pp. 561.

APPENDIX B

MATERIAL BALANCE DATA

TABLE B-1

MATERIAL BALANCE DATA FOR THE PRODUCTION OF $BaCO_3$ FROM CHEMICAL GRADE FRENCH BARITE BLACK ASH

Run BC-1

	Ba (g)	Sr (g)	Fe (g)	F (g)	Ca (g)	Si (g)	Na (g)
Black Ash	16.56	0.10	0.04	0.01	0.06	0.06	0.01
Na_2CO_3	0.00	0.00	0.00	0.00	0.00	0.00	6.78
Residue	0.03	0.00	0.04	0.00	0.02	0.03	0.00
Barren	0.03	0.02	0.00	0.00	0.01	0.00	6.72
$BaCO_3$	16.25	0.08	0.00	0.01	0.04	0.02	0.07
% Recovery in $BaCO_3$	98.13	80.00	0.00	100.00	66.67	33.33	1.03
% Recovery Total	98.49	100.00	100.00	100.00	116.67	83.33	100.00

METHOD DESCRIPTION:

$BaCO_3$ Precipitated @ 80°C Using Na_2CO_3

TABLE B-2

MATERIAL BALANCE DATA FOR THE PRODUCTION OF $BaCO_3$ FROM FLOTATION CONCENTRATE MIXTURE BLACK ASH FC-1 TO 8 BLEND

Run BC-2

	Ba (g)	Sr (g)	Fe (g)	F (g)	Ca (g)	Si (g)	Na (g)
Black Ash	16.23	0.35	0.04	0.17	0.44	0.08	0.01
Na_2CO_3	0.00	0.00	0.00	0.00	0.00	0.00	6.80
Residue	0.40	0.04	0.04	0.14	0.26	0.04	0.00
Barren	0.01	0.01	0.00	0.01	0.11	0.01	6.75
$BaCO_3$	15.69	0.33	0.00	0.01	0.05	0.01	0.06
% Recovery in $BaCO_3$	96.67	94.29	0.00	5.88	11.36	12.50	0.88
% Recovery Total	99.20	105.71	100.00	94.12	95.45	75.00	100.00

METHOD DESCRIPTION:

$BaCO_3$ Precipitated @ 80°C Using Na_2CO_3

TABLE B-3

MATERIAL BALANCE DATA FOR THE PRODUCTION OF $BaCO_3$ FROM TABLE # 23 CONCENTRATE MIDDLE # 1 AND # 2 BLACK ASH

Run BC-3

	Ba (g)	Sr (g)	Fe (g)	F (g)	Ca (g)	Si (g)	Na (g)
Black Ash	15.61	0.36	0.04	0.10	0.39	0.08	0.01
Na_2CO_3	0.00	0.00	0.00	0.00	0.00	0.00	6.81
Residue	0.40	0.05	0.04	0.07	0.22	0.03	0.00
Barren	0.01	0.01	0.00	0.01	0.11	0.02	6.76
$BaCO_3$	15.18	0.33	0.00	0.01	0.04	0.01	0.06
% Recovery $BaCO_3$	97.25	91.67	0.00	10.00	10.26	12.50	0.88
% Recovery	99.87	105.56	100.00	90.00	94.87	75.00	100.00

METHOD DESCRIPTION:

$BaCO_3$ Precipitated @ 80°C Using Na_2CO_3

TABLE B-4

MATERIAL BALANCE DATA FOR THE PRODUCTION OF $BaCO_3$

RUN BCP-1

	Ba (g)	Sr (g)	Ca (g)	Fe (g)	F (g)
Black Ash	16.23	0.38	0.44	0.04	0.17
Residue	0.44	0.05	0.23	0.04	0.14
Barren	0.10	0.02	0.16	0.00	0.01
$BaCO_3$	15.17	0.30	0.02	0.00	0.01
% Recovery in $BaCO_3$	93.47	78.95	4.55	0.00	5.88
% Recovery Total	96.55	97.37	93.18	100.00	94.12

Barite: Black Ash from Flotation Mix Concentrate FC-1 To 8 Blend

METHOD DESCRIPTION:

$BaCO_3$ Precipitated @ 80°C Using Na_2CO_3 and 0.5 g NaOH

TABLE B-5

MATERIAL BALANCE DATA FOR THE PRODUCTION OF $BaCO_3$

RUN BCP-2

	Ba (g)	Sr (g)	Ca (g)	Fe (g)	F (g)
Black Ash	16.23	0.36	0.44	0.04	0.17
Residue	0.48	0.04	0.23	0.04	0.14
Barren	0.45	0.03	0.16	0.00	0.01
$BaCO_3$	14.82	0.30	0.02	0.00	0.02
% Recovery in $BaCO_3$	91.31	83.33	4.55	0.00	11.76
% Recovery Total	97.04	102.78	93.18	100.00	100.00

Barite: Black Ash from Flotation Mix Concentrate FC-1 To 8 Blend

METHOD DESCRIPTION:

$BaCO_3$ Precipitated @ 80°C Using Na_2CO_3 and 1.13 g NaOH

TABLE B-6

MATERIAL BALANCE DATA FOR THE PRODUCTION OF $BaCO_3$

RUN BCP-3

	Ba (g)	Sr (g)	Ca (g)	Fe (g)	F (g)
Black Ash	16.26	0.38	0.44	0.04	0.17
Residue	0.40	0.05	0.23	0.04	0.14
Barren	0.52	0.02	0.17	0.00	0.02
$BaCO_3$	14.78	0.30	0.01	0.00	0.01
% Recovery in $BaCO_3$	90.90	78.95	2.27	0.00	5.88
% Recovery Total	96.56	97.37	93.18	100.00	100.00

Barite: Black Ash from Flotation Mix Concentrate FC-1 To 8 Blend

METHOD DESCRIPTION:

$BaCO_3$ Precipitated @ 80°C Using Na_2CO_3 and 1.13 g NaOH

TABLE B-7

MATERIAL BALANCE DATA FOR THE PRODUCTION OF $BaCO_3$

RUN BCP-4

	Ba (g)	Sr (g)	Ca (g)	Fe (g)	F (g)
Black Ash	16.24	0.38	0.44	0.04	0.17
Residue	0.61	0.05	0.26	0.04	0.14
Barren	0.43	0.01	0.13	0.00	0.02
$BaCO_3$	14.85	0.31	0.05	0.00	0.01
% Recovery in $BaCO_3$	91.44	81.58	11.36	0.00	5.88
% Recovery Total	97.84	97.37	100.00	100.00	100.00

Barite: Black Ash from Flotation Mix Concentrate FC-1 To 8 Blend

METHOD DESCRIPTION:

Leachate Treated With H_2S @ 20°C and 1.21 g NaOH. $BaCO_3$ Precipitated Using Na_2CO_3.

TABLE B-8

MATERIAL BALANCE DATA FOR THE PRODUCTION OF $BaCO_3$

RUN BCP-5

	Ba (g)	Sr (g)	Ca (g)	Fe (g)	F (g)
Black Ash	16.25	0.38	0.44	0.04	0.17
Residue	0.61	0.05	0.26	0.04	0.14
Barren	1.53	0.05	0.14	0.00	0.02
$BaCO_3$	13.76	0.27	0.04	0.00	0.01
% Recovery in $BaCO_3$	84.68	71.05	9.09	0.00	5.88
% Recovery Total	97.85	97.37	100.00	100.00	100.00

Barite: Black Ash from Flotation Mix Concentrate FC-1 To 8 Blend

METHOD DESCRIPTION:

1.25 g Na_2CO_3 Added to Leachate to Precipitate Sr and Ca. Precipitated $BaCO_3$ Using Na_2CO_3.

TABLE B-9

MATERIAL BALANCE DATA FOR THE PRODUCTION OF $BaCO_3$

RUN BCP-6

	Ba (g)	Sr (g)	Ca (g)	Fe (g)	F (g)
Black Ash	16.26	0.38	0.44	0.04	0.17
Residue	1.00	0.05	0.23	0.04	0.14
Barren	1.03	0.02	0.16	0.00	0.02
$BaCO_3$	14.27	0.30	0.02	0.00	0.01
% Recovery in $BaCO_3$	87.76	78.95	4.55	0.00	5.88
% Recovery Total	100.25	97.37	95.35	100.00	100.00

Barite: Black Ash from Flotation Mix Concentrate FC-1 To 8 Blend

METHOD DESCRIPTION:

$BaCO_3$ Precipitated @ 40°C Using Na_2CO_3 and 1.19 g NaOH

TABLE B-10

MATERIAL BALANCE DATA FOR THE PRODUCTION OF $BaCO_3$

RUN BCP-7

	Ba (g)	Sr (g)	Ca (g)	Fe (g)	F (g)
Black Ash	16.24	0.38	0.44	0.04	0.17
Residue	0.52	0.05	0.24	0.04	0.15
Barren	0.46	0.00	0.12	0.00	0.01
$BaCO_3$	14.82	0.32	0.06	0.00	0.01
% Recovery in $BaCO_3$	91.26	84.21	13.64	0.00	5.88
% Recovery Total	97.29	97.37	95.45	100.00	100.00

Barite: Black Ash from Flotation Mix Concentrate FC-1 To 8 Blend

METHOD DESCRIPTION:

1.05 g Urea Added to Leachate to Precipitate Sr and Ca. Precipitated $BaCO_3$ Using Na_2CO_3

TABLE B-11

MATERIAL BALANCE DATA FOR THE PRODUCTION OF $BaCO_3$

RUN BCP-9

	Ba (g)	Sr (g)	Ca (g)	Fe (g)	F (g)
Black Ash	16.23	0.38	0.44	0.04	0.17
Residue	0.80	0.05	0.24	0.04	0.15
Barren	5.39	0.11	0.15	0.00	0.01
$BaCO_3$	9.88	0.21	0.03	0.00	0.01
% Recovery in $BaCO_3$	60.87	55.26	6.82	0.00	5.88
% Recovery Total	99.01	97.37	100.00	100.00	100.00

Barite: Black Ash from Flotation Mix Concentrate FC-1 To 8 Blend

METHOD DESCRIPTION:

$BaCO_3$ Precipitated @ 10°C Using Na_2CO_3 and 1.24 g NaOH

TABLE B-12

MATERIAL BALANCE DATA FOR THE PRODUCTION OF $BaCO_3$

RUN BCP-11

	Ba (g)	Sr (g)	Ca (g)	Fe (g)	F (g)
Black Ash	15.61	0.32	0.39	0.04	0.10
Residue	0.40	0.03	0.22	0.04	0.07
Barren	8.00	0.14	0.16	0.00	0.02
$BaCO_3$	7.44	0.15	0.01	0.00	0.01
% Recovery in $BaCO_3$	47.66	46.88	2.56	0.00	10.00
% Recovery Total	101.47	106.25	100.00	100.00	100.00

Barite: Black Ash from Table # 23 Concentrate

METHOD DESCRIPTION:

Direct Carbonation of Leachate @ 45-50°C Using 4.46 g of CO_2 @ 1 L/min.

TABLE B-13

MATERIAL BALANCE DATA FOR THE PRODUCTION OF $BaCO_3$

RUN BCP-12

	Ba (g)	Sr (g)	Ca (g)	Fe (g)	F (g)
Black Ash	15.61	0.32	0.39	0.04	0.10
Residue	0.39	0.04	0.22	0.04	0.07
Barren	7.55	0.12	0.16	0.00	0.02
$BaCO_3$	7.92	0.17	0.01	0.00	0.01
% Recovery in $BaCO_3$	50.74	53.13	2.56	0.00	10.00
% Recovery Total	101.60	103.13	100.00	100.00	100.00

Barite: Black Ash from Table # 23 Concentrate

METHOD DESCRIPTION:

Direct Carbonation of Leachate @ 45-50°C Using 5.23 g of CO_2 @ 1 L/min.

TABLE B-14

MATERIAL BALANCE DATA FOR THE PRODUCTION OF $BaCO_3$

RUN BCP-13

	Ba (g)	Sr (g)	Ca (g)	Fe (g)	F (g)
Black Ash	15.61	0.32	0.39	0.04	0.10
Residue	0.44	0.04	0.22	0.04	0.07
Barren	6.22	0.10	0.15	0.00	0.02
$BaCO_3$	9.28	0.19	0.02	0.00	0.01
% Recovery in $BaCO_3$	59.45	59.38	5.13	0.00	10.00
% Recovery Total	102.11	103.13	100.00	100.00	100.00

Barite: Black Ash from Table # 23 Concentrate

METHOD DESCRIPTION:

Direct Carbonation of Leachate @ 45-50°C Using 10.45 g of CO_2 @ 1 L/min.

TABLE B-15

MATERIAL BALANCE DATA FOR THE PRODUCTION OF $BaCO_3$

RUN BCP-14

	Ba (g)	Sr (g)	Ca (g)	Fe (g)	F (g)
Black Ash	15.61	0.32	0.39	0.04	0.10
Residue	0.47	0.04	0.22	0.04	0.07
Barren	3.25	0.05	0.15	0.00	0.02
$BaCO_3$	12.17	0.25	0.02	0.00	0.01
% Recovery in $BaCO_3$	77.96	78.13	5.13	0.00	10.00
% Recovery Total	101.79	106.25	100.00	100.00	100.00

Barite: Black Ash from Table # 23 Concentrate

METHOD DESCRIPTION:

Direct Carbonation of Leachate @ 45-50°C Using 20.91 g of CO_2 @ 1 L/min.

TABLE B-16

MATERIAL BALANCE DATA FOR THE PRODUCTION OF $BaCO_3$

RUN BCP-15

	Ba (g)	Sr (g)	Ca (g)	Fe (g)	F (g)
Black Ash	16.23	0.38	0.44	0.04	0.17
Residue	0.47	0.05	0.23	0.04	0.14
Barren	2.34	0.05	0.15	0.00	0.01
$BaCO_3$	12.93	0.27	0.03	0.00	0.02
% Recovery in $BaCO_3$	79.67	71.05	6.82	0.00	11.76
% Recovery Total	96.98	97.37	93.18	100.00	100.00

Barite: Black Ash from Flotation Mix Concentrate FC-1 To 8 Blend

METHOD DESCRIPTION:

Direct Carbonation of Leachate @ 80°C Using CO_2 @ 250 cc/min.

TABLE B-17

MATERIAL BALANCE DATA FOR THE PRODUCTION OF $BaCO_3$

RUN BCP-16

	Ba (g)	Sr (g)	Ca (g)	Fe (g)	F (g)
Black Ash	15.78	0.39	0.33	0.04	0.20
Residue	0.44	0.06	0.14	0.04	0.15
Barren	4.06	0.08	0.14	0.00	0.01
$BaCO_3$	11.21	0.24	0.04	0.00	0.03
% Recovery in $BaCO_3$	71.04	61.54	12.12	0.00	15.00
% Recovery Total	99.56	97.44	96.97	100.00	95.00

Barite: Black Ash from Flotation Mix Concentrate FC-9 to 12 Blend

METHOD DESCRIPTION:

Direct Carbonation of Leachate @ 8°C Using CO_2 @ 250 cc/min.

TABLE B-18

MATERIAL BALANCE DATA FOR BARIUM CARBONATE PRODUCTION

RUN BSP-7

	Ba (g)	Sr (g)	Ca (g)
Black Ash	15.61	0.31	0.38
H_2O Insoluble Residue	0.44	0.04	0.28
Filtered Solution	7.13	0.18	0.03
$BaCO_3$	7.51	0.13	0.01
% Recovery in $BaCO_3$	48.11	41.94	2.63
% Recovery Total	96.60	112.90	84.21

Barite: Bulk Table # 23 Concentrate Middle # 1 and # 2, Black Ash Blend

TABLE B-19

MATERIAL BALANCE DATA FOR BARIUM CARBONATE PRODUCTION

RUN BSP-8

	Ba (g)	Sr (g)	Ca (g)
Black Ash	15.63	0.31	0.38
H_2O Insoluble Residue	0.43	0.04	0.28
Filtered Solution	6.51	0.16	0.01
$BaCO_3$	8.79	0.15	0.01
% Recovery in $BaCO_3$	56.24	48.38	2.63
% Recovery Total	100.64	112.90	78.95

Barite: Bulk Table # 23 Concentrate Middle # 1 and # 2, Black Ash Blend

TABLE B-20

MATERIAL BALANCE DATA FOR PRODUCTION OF $BaCl_2 \cdot 2H_2O$

RUN $BaCl_2 \cdot 2H_2O$ # 1

	Ba (g)	Sr (g)	Ca (g)	F (g)	Na (g)
Black Ash	15.61	0.32	0.38	0.10	0.01
Residue	0.40	0.04	0.22	0.07	0.00
NaCl In.	0.00	0.00	0.00	0.00	12.98
Barren	10.21	0.27	0.15	0.02	12.61
$BaCl_2 \cdot 2H_2O$ # 1	5.36	0.04	0.01	0.01	0.38
% Recovery in $BaCl_2 \cdot 2H_2O$ # 1	34.33	12.50	2.63	10.00	2.93
% Recovery Total	102.30	109.38	100.00	100.00	100.00

Barite: Black Ash from Table # 23 Concentrate

METHOD DESCRIPTION:

100 mls of Saturated NaCl Added to Leachate at 80°C. Allow to Cool to 25°C and Filter

TABLE B-21

MATERIAL BALANCE DATA FOR PRODUCTION OF $BaCl_2 \cdot 2H_2O$

RUN $BaCl_2 \cdot 2H_2O$ # 2

	Ba (g)	Sr (g)	Ca (g)	F (g)	Fe (g)	Na (g)
Black Ash	15.78	0.39	0.33	0.20	0.04	0.01
H_2O Insoluble Residue	0.40	0.05	0.29	0.17	0.04	0.00
$BaCl_2 \cdot 2H_2O$ # 2	15.91	0.33	0.02	0.01	0.00	0.01
% Recovery in $BaCl_2 \cdot 2H_2O$ # 2	100.82	84.62	6.06	5.00	0.00	100.00
% Recovery Total	103.35	97.44	93.94	90.00	100.00	100.00

Barite: Black Ash from Flotation Mix Concentrate FC-9 to 12 Blend

METHOD DESCRIPTION:

30 mls Conc. HCl Added to Leachate at 80°C. Evaporate to Dryness to Crystallize Product.

TABLE B-22

MATERIAL BALANCE DATA FOR PRODUCTION OF $BaCl_2 \cdot 2H_2O$

RUN $BaCl_2 \cdot 2H_2O$ # 3

	Ba (g)	Sr (g)	Ca (g)	F (g)	Fe (g)	Na (g)
Black Ash	15.78	0.39	0.33	0.20	0.04	0.01
H_2O Insoluble Residue	0.57	0.05	0.28	0.18	0.04	0.00
Solids Recovery From Residual H_2O and Acetone Wash of $BaCl_2 \cdot 2H_2O$ # 3	1.20	0.27	0.04	0.00	0.00	0.00
$BaCl_2 \cdot 2H_2O$ # 3	13.91	0.06	0.00	0.00	0.00	0.01
% Recovery in $BaCl_2 \cdot 2H_2O$ # 3	88.15	15.38	0.00	0.00	0.00	100.00
% Recovery Total	99.37	97.44	96.97	90.00	100.00	100.00

Barite: Black Ash from Flotation Mix Concentrate FC-9 to 12 Blend

TABLE B-23

MATERIAL BALANCE DATA FOR PRODUCTION OF $BaCO_3$ FROM $BaCl_2 \cdot 2H_2O$ # 4

RUN $BaCl_2$ # 4

MATERIAL BALANCE DATA (A)

	Ba (g)	Sr (g)	Ca (g)	Fe (g)	F (g)
Black Ash	15.78	0.39	0.33	0.04	0.20
H_2O Insol. Residue	0.57	0.06	0.28	0.04	0.18
Solids Recovered From Residual H_2O and Acetone Wash of $BaCl_2 \cdot 2H_2O$ # 4	0.73	0.27	0.04	0.00	0.00
$BaCl_2 \cdot 2H_2O$ # 4	14.62	0.05	0.00	0.00	0.00
% Recovery in $BaCl_2 \cdot 2H_2O$ # 4	92.65	12.82	0.00	0.00	0.00
% Recovery Total	100.89	97.44	96.97	100.00	90.00

MATERIAL BALANCE DATA (B)

	Ba (g)	Sr (g)	Ca (g)	Fe (g)	F (g)
$BaCl_2 \cdot 2H_2O$ # 4	11.65	0.04	0.00	0.00	0.00
Barren	0.10	0.01	0.00	0.00	0.00
$BaCO_3$	11.47	0.03	0.00	0.00	0.00
% Recovery in $BaCO_3$	98.45	75.00	0.00	0.00	0.00
% Recovery Total	99.31	100.00	100.00	100.00	100.00

Barite: Black Ash from Flotation Mix Concentrate FC-9 to FC-12 Blend

TABLE B-24

MATERIAL BALANCE DATA FOR PRODUCTION OF $BaCO_3$ FROM $BaCl_2 \cdot 2H_2O$ # 5

RUN $BaCl_2$ # 5

MATERIAL BALANCE DATA (A)

	Ba (g)	Sr (g)	Ca (g)	Fe (g)	F (g)
Black Ash	15.78	0.39	0.33	0.04	0.20
H_2O Insol. Residue	0.53	0.05	0.28	0.04	0.18
Solids Recovered From Acetone Wash of $BaCl_2 \cdot 2H_2O$ # 5	0.00	0.00	0.00	0.00	0.00
$BaCl_2 \cdot 2H_2O$ # 5	15.30	0.34	0.03	0.00	0.00
% Recovery in $BaCl_2 \cdot 2H_2O$ # 5	96.96	87.18	9.09	0.00	0.00
% Recovery Total	100.32	100.00	93.94	100.00	90.00

MATERIAL BALANCE DATA (B)

	Ba (g)	Sr (g)	Ca (g)	Fe (g)	F (g)
$BaCl_2 \cdot 2H_2O$ # 5	8.97	0.20	0.02	0.00	0.00
Barren	0.06	0.01	0.00	0.00	0.00
$BaCO_3$	8.91	0.19	0.02	0.00	0.00
% Recovery in $BaCO_3$	99.33	95.00	100.00	0.00	0.00
% Recovery Total	100.00	100.00	100.00	100.00	100.00

Barite: Black Ash from Flotation Mix Concentrate FC-9 to FC-12 Blend

TABLE B-25

MATERIAL BALANCE DATA FOR PRODUCTION OF $BaCl_2 \cdot 2H_2O$

RUN $BaCl_2$ # 6

	Ba (g)	Sr (g)	Ca (g)	Fe (g)	F (g)
Black Ash	15.78	0.39	0.33	0.04	0.20
H_2O Insol. Residue	0.57	0.04	0.26	0.04	0.18
Solids Recovered From Residual H_2O and Acetone Wash of $BaCl_2 \cdot 2H_2O$ # 6	4.60	0.33	0.05	0.00	0.00
$BaCl_2 \cdot 2H_2O$ # 6	9.42	0.00	0.00	0.00	0.00
% Recovery in $BaCl_2 \cdot 2H_2O$ # 6	59.70	0.00	0.00	0.00	0.00
% Recovery Total	92.46	94.87	93.94	100.00	90.00

Barite: Black Ash from Flotation Mix Concentrate FC-9 to FC-12 Blend

TABLE B-26

MATERIAL BALANCE DATA FOR PRODUCTION OF $BaCl_2 \cdot 2H_2O$

RUN $BaCl_2$ # 7

	Ba (g)	Sr (g)	Ca (g)	Fe (g)	F (g)
Black Ash	15.78	0.39	0.33	0.04	0.20
H_2O Insol. Residue	0.56	0.05	0.26	0.04	0.17
Solids Recovered From Residual H_2O and Acetone Wash of $BaCl_2 \cdot 2H_2O$ # 7	2.78	0.30	0.05	0.00	0.00
$BaCl_2 \cdot 2H_2O$ # 7	12.20	0.01	0.00	0.00	0.00
% Recovery in $BaCl_2 \cdot 2H_2O$ # 7	77.31	2.56	0.00	0.00	0.00
% Recovery Total	98.48	92.31	93.94	100.00	85.00

Barite: Black Ash from Flotation Mix Concentrate FC-9 to FC-12 Blend

TABLE B-27

MATERIAL BALANCE DATA FOR PRODUCTION OF $Ba(NO_3)_2$

RUN $Ba(NO_3)_2$ # 2

	Ba (g)	Sr (g)	Ca (g)	Fe (g)	F (g)
$BaCO_3$	6.61	0.14	0.02	0.00	0.01
Barren	0.63	0.12	0.02	0.00	0.01
$Ba(NO_3)_2$ # 2	5.98	0.02	0.00	0.00	0.00
% Recovery in $Ba(NO_3)_2$ # 2	90.47	14.29	0.00	0.00	0.00
% Recovery Total	100.00	100.00	100.00	100.00	100.00

Barite: Black Ash from Flotation Mix Concentrate FC-9 to 12 Blend

METHOD DESCRIPTION:

19 mls Conc. HNO_3 Added to 10 g of $BaCO_3$ (BCP-9) in 120 mls D.D. Water @ 80°C.

TABLE B-28

MATERIAL BALANCE DATA FOR PRODUCTION OF $Ba(NO_3)_2$

RUN $Ba(NO_3)_2$ # 3

	Ba (g)	Sr (g)	Ca (g)	Fe (g)	F (g)
Black Ash	15.78	0.39	0.33	0.04	0.20
H_2O Insol. Residue	0.49	0.04	0.28	0.04	0.18
Solids Recovered From Residual H_2O and Acetone Wash	1.55	0.32	0.03	0.00	0.00
$Ba(NO_3)_2$ # 3	13.83	0.02	0.00	0.00	0.00
% Recovery in $Ba(NO_3)_2$ # 3	87.64	5.12	0.00	0.00	0.00
% Recovery Total	100.57	97.44	93.94	100.00	90.00

Barite: Black Ash from Flotation Mix Concentrate FC-9 to FC-12

TABLE B-29

MATERIAL BALANCE DATA FOR PRODUCTION OF $Ba(NO_3)_2$

RUN $Ba(NO_3)_2$ # 4

	Ba (g)	Sr (g)	Ca (g)	Fe (g)	F (g)
Black Ash	15.78	0.39	0.33	0.04	0.20
H_2O Insol. Residue	0.58	0.04	0.28	0.04	0.18
$Ba(NO_3)_2$ # 4	14.76	0.37	0.03	0.00	0.00
% Recovery in $Ba(NO_3)_2$ # 4	93.54	94.87	9.09	0.00	0.00
% Recovery Total	97.15	105.13	93.94	100.00	90.00

Barite: Black Ash from Flotation Mix Concentrate FC-9 to FC-12 Blend

TABLE B-30

MATERIAL BALANCE DATA FOR PRODUCTION OF $Ba(NO_3)_2$

RUN $Ba(NO_3)_2$ # 5

	Ba (g)	Sr (g)	Ca (g)	Fe (g)	F (g)
Black Ash	15.78	0.39	0.33	0.04	0.20
H_2O Insol. Residue	0.57	0.05	0.28	0.04	0.18
Solids Recovered From Residual H_2O and Acetone Wash	1.72	0.31	0.03	0.00	0.00
$Ba(NO_3)_2$ # 5	13.09	0.02	0.00	0.00	0.00
% Recovery in $Ba(NO_3)_2$ # 5	82.95	5.13	0.00	0.00	0.00
% Recovery Total	97.47	97.44	93.94	100.00	90.00

Barite: Black Ash from Flotation Mix Concentrate FC-9 to FC-12 Blend